

**Online supplement for Secondary organic aerosol  
formation from gasoline passenger vehicle emissions  
investigated in a smog chamber**

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## Methods and material

### Heated inlet system

The raw exhaust was sampled from the exhaust pipe using a partial flow technique. The sample was taken through a flexible stainless steel tube with a length of 1.5 m and an inner diameter of 20 mm. The flexible tube was heated to 80 °C, which was higher than the exhaust temperature (typically 70 °C). Downstream the ejector the diluted exhaust was transferred to the smog chamber in a stainless steel pipe heated to 120 °C. The length of this pipe was 6 m and the inner diameter was 10 mm.

### UV-spectrum

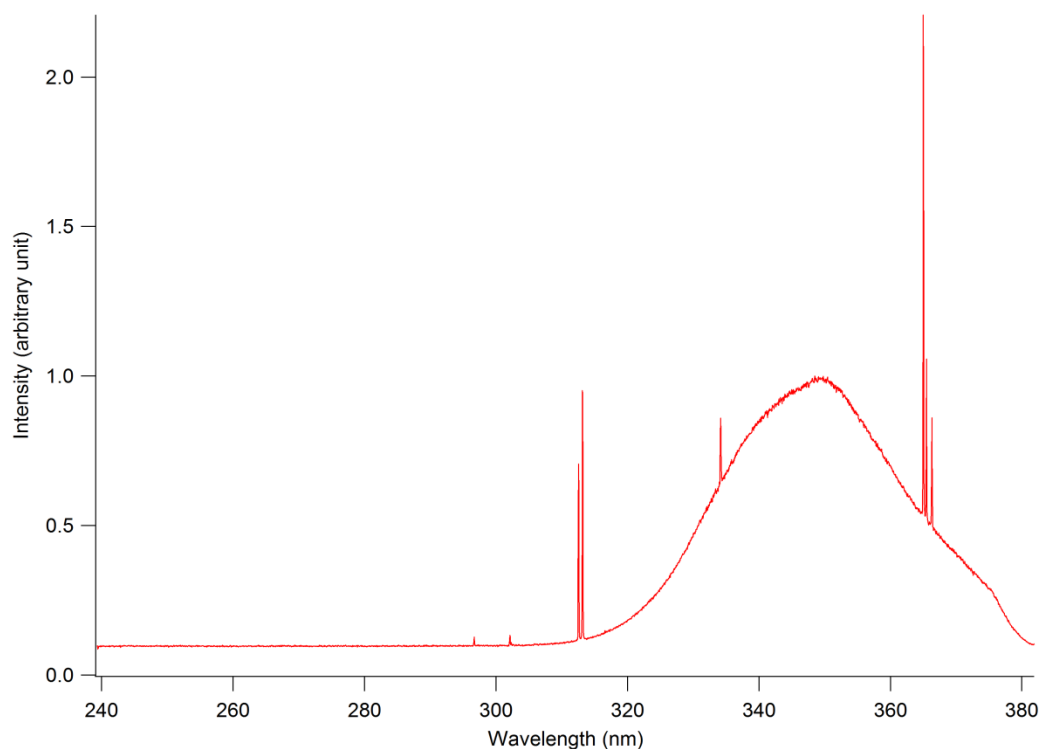


Figure S1. The measured UV-intensity spectrum from the black-lights used in the smog chamber.

### Cleaning of the Teflon chamber

After a finished experiment the smog chamber was purged with filtered pressurized air. After this the chamber was cleaned with >1 ppm ozone for at least 5 h. During the cleaning procedure the UV-radiation was operated in 30 minute cycles without chamber cooling,

raising the smog chamber temperature to above 40 °C. This facilitates evaporation and degradation of organic contaminants on the chamber walls. The chamber was finally purged with dry pressurized air for several hours. Before each experiment, particle (AMS, SMPS) and gas (NO<sub>x</sub>, O<sub>3</sub> and PTR-MS (when available)) phase instruments sampled from the smog chamber to make sure that smog chamber was sufficiently clean. PTR-MS measurements during the blank experiment show a total concentration of light aromatics of less than 1 ppb.

## Vehicles

In total six gasoline passenger vehicles were tested at cold idling, the three cars selected represented three different European emission classes and had also suitable VOC to NO<sub>x</sub> ratios. All tested vehicles used three way catalysts. In the cold idling case, the cars were driven on a specified circuit until an engine temperature of 55 ±5 °C was reached. In this case neither the engine nor the catalyst had reached optimum operating temperature. Figure S2 shows the concentration of total-hydrocarbons during a cold idling experiment (I3), measured with a flame ionization detector (FID), calibrated with isobutene. In most experiments there was no systematic increase or decrease in the THC levels in the exhaust with time.

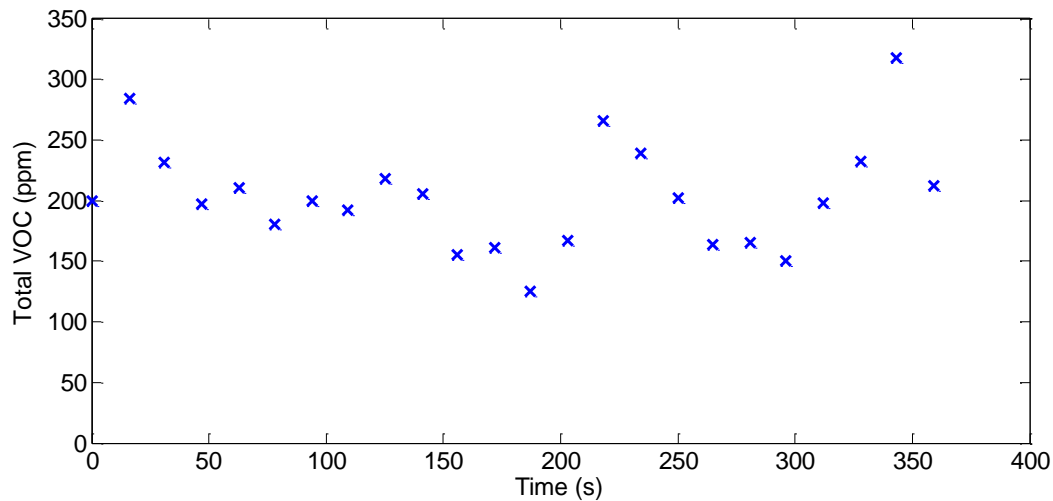
Table S1. Technical data of the three gasoline light duty vehicles used

European emission standard class	Power (kW)	Odometer (km)	Displacement (cm <sup>3</sup> )	Weight (kg)
II	118	220 000	1948	1400
III	115	180 000	1998	1426
IV	48	60 000	998	1050

1 Table S2. Experimental conditions

Experiment	Total exhaust dilution	Ambient temperature °C
I1	31	-2
I2	109	-4
I3	90	-2
I4	78	-5
I5	27	3
S1	~1600	-5

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4 Figure S2: The concentration of Total Hydrocarbons in the undiluted exhaust as a function of time,  
5 experiment I3. The gasoline exhaust was added to the chamber for six minutes under cold idling  
6 conditions from an initial engine temperature of 55 C using the Euro II vehicle.

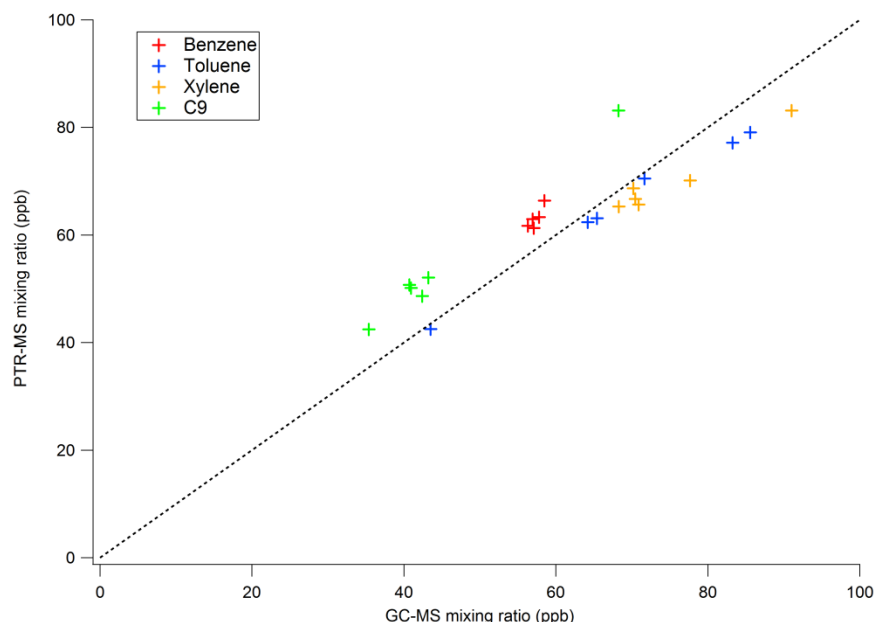
7 **Experimental procedure**

8 During the experiments the surrounding steel chamber was constantly flushed with pure air (5  
9 air exchanges/h). To avoid leaks into the smog chamber from the surrounding steel room, an  
10 overpressure was maintained in the smog chamber by manually elevating the floor and  
11 lowering the roof of the smog chamber.

12 **Results**

13 Figure S2 shows a comparison between PTR-MS and GC-MS measurements. The average  
14 ratio between the PTR-MS and GC-MS mixing ratio for each light aromatic is slightly lower

1 than 1 for toluene and xylenes, while it is higher for benzene and C<sub>9</sub> aromatics where the  
2 latter has an average ratio of 1.2.



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5 Figure S3. A comparison between PTR-MS and GC-MS for C<sub>6</sub>-C<sub>9</sub> aromatics measured in the  
6 smog chamber. The broken line shows a ratio of 1.

7 The PTR-MS method is based on reactions of hydronium ions ( $\text{H}_3\text{O}^+$ ) with gaseous  
8 compounds having a larger proton affinity than that of  $\text{H}_2\text{O}$ , which results in a non-  
9 dissociative proton transfer to a majority of the VOCs. The PTR-MS consists of a discharge  
10 ion source to produce the primary ions, a drift-tube reactor, where the proton transfer reaction  
11 between  $\text{H}_3\text{O}^+$  and the target VOC takes place and a quadrupole mass spectrometer for the  
12 detection of reagent and product ions. Evidence of weak fragmentation of C<sub>7</sub> and C<sub>8</sub>  
13 compounds was found as suggested by a slightly larger ratio of PTR-MS to GC-MS for  
14 benzene than for toluene and xylenes (Jobson et al., 2010).

1    Table S3. Chemical composition of the gasoline fuel and the undiluted gasoline exhaust.

Compound	Fuel (ng $\mu\text{g}^{-1}$ )	Exhaust <sup>a</sup> (mg $\text{m}^{-3}$ )
methyl tert-butyl ether (MTBE)	12.3	-
ethyl tert-butyl ether (ETBE)	0.5	-
benzene	11.7	13.96
toluene	117.9	16.02
ethylbenzene	19.0	2.83
p/m-xylene	72.2	14.49
o-xylene	21.1	5.90
propylbenzene	5.0	1.06
3-ethyltoluene	13.6	4.32
4-ethyltoluene	5.8	1.99
1,3,5-trimethylbenzene	6.8	2.42
2-ethyltoluene	4.6	1.76
1,2,4-trimethylbenzene	18.8	10.95
1,2,3-trimethylbenzene	3.2	1.72
2,2,4-trimethylpentane	112.4	1.14
hexane	68.3	2,13
heptane	20.7	2.67
octane	4.0	1.17
sulfur	<0.01	-
ethanol	5 vol%	-

2    <sup>a</sup>Average for experiment I1-I3

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Table S4.  $f_{43}$  and  $f_{44}$  fractions, reacted mass fractions and yield relative to m-xylene for the pure precursors presented in figure 8. These were used for calculations of the expected  $f_{43}$  and  $f_{44}$  of gasoline exhaust assuming that all SOA originated from C<sub>6</sub>-C<sub>9</sub> light aromatic compounds.

Compound	$f_{43}$	$f_{44}$	Reacted mass fraction of (C <sub>6</sub> -C <sub>9</sub> ) LA (average of I1 and I2)	Reference
benzene	0.03	0.12	0.011	Ng et al., 2010
toluene	0.130	0.120	0.115	Chhabra et al., 2011
ethylbenzene	0.023	0.122	0.016	Sato et al., 2010
m/o/p-xylene	0.170	0.095	0.344 <sup>a</sup>	Exp. P2 this study
1,3,5-trimethylbenzene	0.175	0.055	0.100	Ng et al., 2010
1,2,4-trimethylbenzene	0.197	0.088	0.230	Derived from experiment P1
1,2,3-trimethylbenzene	0.197	0.088	0.047	Assumed to be same as 1,2,4-tmb
2/3/4-ethyltoluene and propyl benzene	0.110	0.105	0.137	Assumed as the mean of ethylbenzene and 1,2,4-trimethylbenzene
naphthalene <sup>b</sup>	0.01	0.1	-	Chhabra et al., 2011

<sup>a</sup>All xylenes are assumed to have the same  $f_{43}$  and  $f_{44}$  as measured for m-xylene in exp. P2.

<sup>b</sup>Not included in calculation, given here for reference.

#### **Expected $f_{43}$ and $f_{44}$ assuming additive SOA composition and yield for C<sub>6</sub>-C<sub>9</sub> Light aromatics**

First we note that the  $f_{43}$  and  $f_{44}$  fractions for m-xylene in experiment P2 were within 0.02 of values from several studies in the literature (Ng et al. 2010, Chhabra et al. 2011, Loza et al. 2012) suggesting that these measurements are typically repeatable between instruments and set-ups. In Table S4 we list literature values for the most important C<sub>6</sub>-C<sub>9</sub> light aromatic precursors, for compounds with no available literature data we had to make assumptions based on the structure of the component. For example, the three xylene isomers were assumed to have the same  $f_{43}$  and  $f_{44}$  fractions as found for m-xylene. This is supported by a study

with the potential aerosol mass chamber which showed that the  $f_{43}$  and  $f_{44}$  fractions of SOA from p- and m- xylene varied by less than 0.01 (Kang et al. 2011). The  $f_{43}$  and  $f_{44}$  values for 1,2,4-trimethylbenzene were derived from experiment P1 (precursor mixture of 1,2,4 TMB, m-xylene and toluene), where 1,2,4 TMB constituted more than 60% of the reacted light aromatics. We used the  $f_{43}$ ,  $f_{44}$  and yields for toluene and m-xylene given in Table S4 and assumed that the mixed SOA was additive in terms of yield and composition.

Finally, we estimated the expected  $f_{43}$ ,  $f_{44}$  in each gasoline exhaust experiment if assuming additive yield and composition. The SOA contribution from each component was first calculated from the reacted mass fraction and yield using the high and low yield aromatic classes from Odum et al. (1997). Then the  $f_{43}$  and  $f_{44}$  fractions were calculated as the weighted sum of the thirteen different components in table S4. The resulting “expected”  $f_{43}$  and  $f_{44}$  are given in table S5.

Table S5. The expected and measured  $f_{43}$  and  $f_{44}$  for the six gasoline exhaust experiments. The expected  $f_{43}$  and  $f_{44}$  figures are based on the assumption that the SOA was produced only from light aromatics ( $C_6$ - $C_9$ ) and that the mass spectra of the gasoline exhaust can be calculated as the weighted mean of the SOA from each precursor. The  $f_{43}$  and  $f_{44}$  figures for 13 pure  $C_6$ - $C_9$  light aromatic precursors (table S4) are used together with the GC-MS data of the reacted concentration for those precursors to calculate the expected  $f_{43}$  and  $f_{44}$ . Benzene, toluene, ethyl-benzene, propyl benzene and the ethyl-toluenes were assumed to have twice as high yield as m-xylene (Odum et al., 1997).

Exp.	Expected $f_{43}$	Expected $f_{44}$	Measured <sup>a</sup> $f_{43}$	Measured <sup>a</sup> $f_{44}$	Maximum fraction of $C_6$ - $C_9$ contribution to SOA <sup>b</sup>
I1	0.145	0.099	0.088	0.114	0.61
I2	0.148	0.097	0.090	0.130	0.61
I3	0.158	0.093	0.086	0.090	0.54
I4	0.138	0.103	0.080	0.130	0.58
I5	0.157	0.097	0.081	0.107	0.52
S1	0.142	0.101	0.148	0.095	1.04

<sup>a</sup>POA subtracted

<sup>b</sup>Based on the ratio between the measured and expected  $f_{43}$ .



Table S6. Estimations of potential SOA formed from C<sub>10</sub>, C<sub>11</sub> light aromatics and naphthalene. For C<sub>10</sub> light aromatics, the reacted concentration was estimated from PTR-MS measurements. For C<sub>11</sub> light aromatics and naphthalene the initial concentration was first estimated using PTR-MS and the reacted concentration was calculated using  $k_{OH} = 5.67 \times 10^{-11}$  (C<sub>11</sub>) and  $k_{OH} = 2.44 \times 10^{-11}$  (naphthalene) (The Master Chemical Mechanism). The yield curves for C<sub>10</sub> and C<sub>11</sub> were assumed to be identical to m-xylene (according to the fit in figure 5), while the yield for naphthalene is assumed to be three times the yield for m-xylene.

Exp. Id	Initial concentration of C <sub>10</sub> / C <sub>11</sub> / naphthalene (ppb)	Reacted conc. C <sub>10</sub> / C <sub>11</sub> / naphthalene (µg m <sup>-3</sup> )	Potentially formed SOA C <sub>10</sub> / C <sub>11</sub> / naphthalene (µg m <sup>-3</sup> )
I1	13.4/11./2.8	30.7/2.6/3.6	2.5/0.2/0.9
I2	17.7/1.6/4.4	40.1/5.9/6.0	4.6/0.7/2.1
S1	4.4/0.2/0.2	12.6/0.4/0.2	0.8/<0.1/<0.1

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